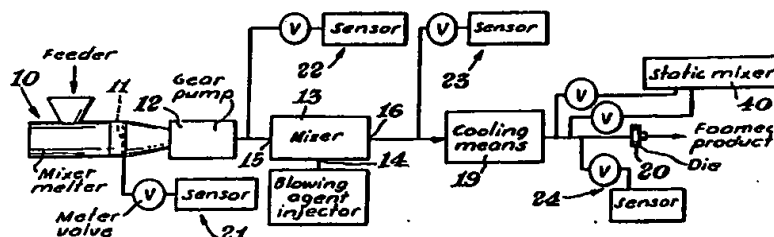




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : B29B 7/30, 7/32, 7/46 C08J 9/12, 9/14, 9/30	A1	(11) International Publication Number: WO 90/07407 (43) International Publication Date: 12 July 1990 (12.07.90)
(21) International Application Number: PCT/US89/05865 (22) International Filing Date: 22 December 1989 (22.12.89) (30) Priority data: 290,598 27 December 1988 (27.12.88) US (71) Applicant: THE DOW CHEMICAL COMPANY [US/ US]; 2030 Dow Center, Abbott Road, Midland, MI 48640 (US). (72) Inventors: KORB, Jean, G. ; 32, rue de la Loire, F-67800 Hoenheim (FR). HARFMANN, Walter, R. ; 1360 Ac- worth Due West Rd., Kennesaw, GA 30144 (US). (74) Agent: MACLEOD, Roderick, B.; The Dow Chemical Company, P.O. Box 1967, Midland, MI 48641-1967 (US).		(81) Designated States: BR, FI, NO. Published <i>With international search report.</i>

(54) Title: METHOD AND APPARATUS FOR PREPARING THERMOPLASTIC FOAM



(57) Abstract

Thermoplastic foam is prepared by a continuous process comprising melt mixing thermoplastic resin (10); pressurizing the resin melt (12); introducing blowing agent (14); cooling and depressurizing the resultant gel (19); and either foaming and forming the gel to form a foamable composition (20). The process temperature is maintained substantially independently of the flow rate of the resin melt and gel at below that at which substantial deprecation of the resin gel occurs. The process has particular application to rubber-modified polystyrene or rubber-modified polyethylene resin foam compositions containing a fire retardant.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MG	Madagascar
AU	Australia	FI	Finland	ML	Mali
BB	Barbados	FR	France	MR	Mauritania
BE	Belgium	GA	Gabon	MW	Malawi
BF	Burkina Faso	GB	United Kingdom	NL	Netherlands
BG	Bulgaria	HU	Hungary	NO	Norway
BJ	Benin	IT	Italy	RO	Romania
BR	Brazil	JP	Japan	SD	Sudan
CA	Canada	KP	Democratic People's Republic of Korea	SE	Sweden
CF	Central African Republic	KR	Republic of Korea	SN	Senegal
CG	Congo	LI	Liechtenstein	SU	Soviet Union
CH	Switzerland	LK	Sri Lanka	TD	Chad
CM	Cameroon	LU	Luxembourg	TG	Togo
DE	Germany, Federal Republic of	MC	Monaco	US	United States of America
DK	Denmark				

METHOD AND APPARATUS FOR PREPARING
THERMOPLASTIC FOAM

The present invention relates generally to a method and an apparatus especially useful for low temperature preparation of thermoplastic foam compositions. The present invention also relates to
5 novel foam compositions containing highly desirable amounts of rubber and fire retardant.

Commercial preparation of thermoplastic foam composition was disclosed in the 1930's. An early
10 disclosure, Munter et al., U.S. Patent No. 2,023,204, teaches a batch process for preparation of foam boards wherein thermoplastic resin is melted in a pressurized vessel containing a blowing agent. A valve opening in
15 the vessel allows the resin to foam directly into the outside air or into a shaping vessel.

With the advent of continuous foam processing utilizing extruder apparatuses, an improved foam product was made possible at lower cost thus resulting in
20 widespread commercial use. Numerous processes were developed in efforts to improve the extruder apparatus and hence improve methods of preparation.

25

-2-

McIntire, U.S. Patent No. 2,515,250 discloses a continuous process for making thermoplastic foam compositions and an apparatus for preparing foam compositions which includes a separate
5 temperature/pressure regulating zone located between an extruder and a pressurized storage vessel.

Winstead, U.S. Patent No. 3,830,901 discloses a continuous process for extruding thermoplastic foam
10 compositions and an apparatus consisting of an extruder, a gear pump, a cooling zone and a die.

Presently, commercial production of thermoplastic foam typically utilizes an apparatus in which an
15 extruder is a means for melting and pressurizing a resin to a resin melt, and mixing additives and blowing agents with the melt to form a resin gel. Subsequently the gel is forwarded through a cooling-depressurizing means and a foaming means.
20

The production of thermoplastic resin foam must necessarily be carried out above the glass transition temperature (T_g) or the melt temperature (T_m) of the resin. Above the T_g or T_m there exists an optimum
25 temperature range for producing foam compositions possessing good structural integrity. Among the parameters which determine the optimum operational temperature are the weight average molecular weight (MW) distribution of the resin and the nature and amount of
30 the additives in the resin gel. For example, the optimally desirable temperature range for processing a polystyrene resin gel of weight average MW of approximately 200,000 having a glass transition
35 temperature of about 100°C (degrees centigrade) is in the range of about 140°C to about 195°C. Other

-3-

temperature ranges apply to other resins and other resin/additive combinations.

5 In commonly used commercial processes for production of foam compositions at optimum production rates, the resin gel temperature ranges exceed optimum temperature ranges. For example, the temperature range for processing polystyrene gel usually ranges from about 200°C to about 250°C. The higher temperatures above 10 200°C occur when output rates exceed about 200 lbs/hr (90 kg/hr). The high gel temperatures at high production rates are attributed to thermal energy generated by shear forces created by extruder screw movement. Gel temperatures in excess of that required 15 for melting the resin cause certain problems.

One problem arises when a fire retardant is introduced into the resin melt. At temperatures above about 190°C, commonly used halogenated fire retardants 20 such as hexabromocyclododecane (HBCD), pentabromomono-chlorocyclohexane (PBCH) and tetrabromobisphenol A (TBBA) exhibit sufficient degradation resulting in a significant amount of free radical degradation product. 25 The free radicals react with the polymeric backbone of the resin gel resulting in chain scissions which reduce the weight average molecular weight (MW) of the resin. A lower MW resin undesirably effects the structural properties of the resultant foam composition.

30 One technique commonly employed to compensate for MW loss, is to initiate the foam-making process with a resin of higher average MW than the desired MW of the resultant foam composition. However, the use of higher 35 MW resin does not completely solve temperature related degradation problems. As the MW of the resin increases,

-4-

the viscosity of resin gel increases causing an increase in the shear forces in the extruder mixing chamber. In turn, increased shear forces create an increase in the resin gel temperature causing a further degradation in additives and resin.

A further drawback to high temperature processing concerns limitations on the types of foam compositions which can be produced. For example, foam compositions containing a high rubber content and also containing a desirably high content of a preferred fire retardant are not easily produced at high temperatures. The rubber phase of the resin gel degrades readily and halogenated fire retardants enhance the degradation process.

Because of the above-listed limitations and problems imposed on the preparation of foam using an extruder it would be highly desirable to find an alternative method for preparing certain thermoplastic foam compositions.

The present invention provides a solution to the problems encountered in the preparation of thermoplastic resin foam at high throughput rates which cause undesirably high temperature ranges. Improved rubber-modified foam compositions can be produced at lower temperatures without sacrificing throughput rates by utilizing the apparatus and method of the present invention.

Briefly there are three major aspects to the invention. In one aspect, the present invention relates to novel foam products. For example, the novel foam product can be a thermoplastic resin foam composition

-5-

c mprising a rubber-modified p lyethylene resin r a
rubber-modified polystyrene resin and 0.01 weight
percent to 5 weight percent by resin weight of a fire
retardant wherein the rubber-modified resin has
5 dispersed rubber particles in a polymeric matrix in an
amount of 3 weight percent to 30 weight percent of the
total resin weight. Other aspects of the invention
relate to a method and an apparatus for continuous
preparation of thermoplastic foam compositions; which
10 method and apparatus demonstrate improved energy-
efficient preparation of foam at low temperature ranges
wherein the resin melt and resin gel temperatures are
maintained essentially independently of the throughput
rate. Thus, low temperature processing of foams is
15 provided at high output rates.

In another aspect the present invention
comprises a continuous method for preparation of a
thermoplastic resin foam or foamable composition
20 sequentially comprising the steps of:

(a) melting and mixing at least one
thermoplastic resin to form a resin melt, the mixing
25 process being carried out without applying shear forces
of sufficient thermal energy to cause a localized rise
in temperature to a temperature at which substantial
degradation of the resin melt occurs;

(b) pressurizing to and maintaining the resin
30 melt at a pressure sufficient to permit introduction of
one or more blowing agents into the resin melt at a
temperature below the temperature at which substantial
degradation of the resin melt occurs;

35

-6-

(c) introducing and dispersing one or more blowing agents substantially throughout the resin melt to form a resin gel at a temperature above the glass transition temperature or the melt temperature of the thermoplastic resin and below a temperature at which substantial degradation of the resin gel occurs; and

(d) cooling and depressurizing the resin gel, the depressurizing being carried out at a sufficiently cool temperature for formation of a foam composition with structural integrity, and the cooling and depressurizing being carried out substantially at the same time;

(e) either foaming and forming the resin gel to form a solid foam composition or foaming the resin gel to form a solid foamable composition;

the recited steps being carried out continuously in a series of stages with the temperature of the resin melt and gel being maintained substantially independently of the flow rate of the resin melt and gel advancing through and between the stages.

The method for preparation of thermoplastic resin foam compositions of the present invention provides an alternative to presently-used extrusion methods and a considerable improvement over batch methods. Optimum production rates can be maintained while allowing processing at lower gel temperatures.

In a still further aspect the present invention relates to an apparatus for continuous production of thermoplastic resin foam or foamable compositions by the method of this invention, said apparatus comprising:

-7-

(a) melting-mixing means for melting and mixing at least one thermoplastic resin to form a resin melt, the melting-mixing means having moving mixing elements and being adapted by the spacing between the moving mixing elements and interaction thereof to accomplish substantial mixing of the resin melt essentially without shear forces of sufficient thermal energy to cause a localized rise in the temperature of the resin melt to greater than 150°C above the glass transition temperature or melt temperature of the resin; the melting-mixing means having an inlet for the resin and an outlet for the resin melt, and means for causing the resin melt to discharge from the outlet;

(b) pump means for pressurizing the resin melt to a pressure in the range of 1000 pounds per square inch gauge (psig) (7000 kiloPascals gauge (kPag)) to 10,000 psig (70,000 kPag), the pump means having an inlet and an outlet and means for metering the resin melt through the outlet;

(c) pressurized mixing means for dispersing one or more blowing agents into the resin melt within a pressurized zone to form a resin gel, the pressurized mixing means being provided with an inlet for introducing the blowing agents, an inlet for the resin melt, and an outlet for discharging the resin gel under pressure;

(d) cooling-depressurizing means for concurrently cooling the resin gel within a pressurized zone and discharging the resin gel through a foam-forming die orifice means to form a solid foam composition; the cooling-depressurizing means having an

inlet for receiving the resin gel under pressure and an outlet for the cooled gel; and

(e) conduit means providing fluid
5 communication respectively and sequentially between the outlet of the melting-mixing means and the inlet of the pump means, between the outlet of the pump means and the inlet of the pressurized mixing means, between the
10 outlet of the pressurized mixing means and the inlet of the cooling-depressurizing means and between the outlet of the cooling-depressurizing means and the foam-forming die orifice means.

Referring to the drawings, Fig. 1 is a
15 schematic diagram illustrating an embodiment of the apparatus of the present invention. This combination of equipment means produces continuously extruded thermoplastic foam compositions as further explained in
20 Example 1;

Fig. 2 is a schematic diagram illustrating
another embodiment of the apparatus of the present invention in which the means for pressurized mixing of
25 blowing agents in the resin melt has been modified to comprise a combination of two modes for pressurized mixing means as further explained in Example 3.

One embodiment of the invention comprises novel
30 rubber-modified polystyrene resin foam compositions and rubber-modified polyethylene resin foam compositions having about 0.01 weight percent to about 5 weight percent by resin weight of a fire retardant, preferably
35 about 1 weight percent to about 3 weight percent, with the balance of the foam composition being rubber-modified polystyrene resin or rubber-modified

polyethylene resin and any other additives, including blowing agents. The resin has dispersed rubber, preferably polymeric butadiene particles in a polymeric matrix in an amount of about 3 weight percent to about 5 30 weight percent of the resin weight, preferably about 3 weight percent to about 22 weight percent, more preferably about 3 weight percent to about 16 weight percent. The fire retardant preferably is a halogenated compound from the group consisting of HBCD, 10 PBCH and TBBA. The blowing agents and additives described in this specification are used in amounts that are well-known in the art.

The foam composition is essentially a closed 15 cell rigid foam with a density ranging from at least about 1 pound per cubic foot (lb/ft^3) (16 kilograms per cubic meter (kg/m^3)) to about 10 lb/ft^3 (160 kg/m^3), preferably about 1.0 lb/ft^3 (16 kg/m^3) to about 20 5.0 lb/ft^3 (80 kg/m^3), more preferably about 1.0 lb/ft^3 (16 kg/m^3) to about 2.5 lb/ft^2 (40 kg/m^3). The cell diameter ranges from about 0.1 mm (millimeter) to about 4 mm, preferably from about 0.2 mm to about 2.5 mm, more preferably from about 0.2 mm to about 1 mm.

25 Among the thermoplastic resins which can be utilized to produce corresponding foam compositions using the apparatus and method of the present invention are polymers such as styrenic polymers disclosed in Suh, 30 U.S. Patent No. 4,085,073. Other olefinic polymers and copolymers can be foamed using this process such as polyethylene, low density polyethylene (LDPE), linear low density polyethylene (LLDPE), ultra low density polyethylene, copolymers of ethylene/vinyl acetate, high 35 density polyethylene (HDPE), copolymers of ethylene/acrylic acid (EAA), polypropylene (PP),

polyesters, polycarbonat s rubber modified p lystyrenes,
acrylonitrile-butadiene-polystyrene (ABS), polyvinyl
chloride (PVC), polyvinylidene copolymers, high bromine
containing rubber modified polystyrene, ethylenic
5 ionomers, styrenic ionomers and mixtures thereof.

Among the blowing agents which can be used are
halocarbons and halohydrocarbons such as chlorofluoro-
carbons and fluorocarbons, chlorofluorohydrocarbons and
10 fluorohydrocarbons, water, carbon dioxide, halogenated
lower alkyls such as methyl and ethyl chloride, lower
alkyls containing one to about 6 carbon atoms such as
butane, nitrogen gas, and oxygen gas. Preferred blowing
agents comprise the halohydrocarbons such as
15 fluorohydrocarbons or chlorofluorohydrocarbons
containing at least one hydrogen atom attached to a
carbon atom, water, carbon dioxide, methyl chloride and
ethyl chloride and mixtures thereof.

20 Additives which may be mixed with the
thermoplastic resin to make a thermoplastic resin melt
include fire retardants, cell nucleating agents, cell
enlarging agents, plasticizers, acid scavengers,
25 colorants, antioxidants, lubricants, antistatic agents
and corrosion inhibitors among others.

Among the fire retardants which can be used and
are preferred are bromine containing cycloalkyls, most
30 preferably HBCD, PBCH, and TBBA.

Cell nucleating agents include but are not
limited to talc, indigo, phthalocyanine blue, magnesium
oxide and metal stearates. Preferred cell nucleating
35 agents include talc, indigo, magnesium oxide and metal

-11-

stearates. The more preferred cell nucleating agent is talc.

5 Among the cell enlarging agents are waxy materials, LDPE, and LLDPE. Preferred cell enlarging agents comprise LDPE and LLDPE.

10 Among the plasticizers are saturated aliphatic oils containing about 1 to about 22 carbon atoms. Preferred plasticizers are diacetyl phthalate, dihexyl phthalate, and saturated aliphatic oils such as mineral oil.

15 Acid scavengers include but are not limited to magnesium oxide and tetrasodiumpyrophosphate (TSPP).

20 A novel aspect of the invention is that the melting-mixing and pressurizing of the resin melt and any dispersion therein of blowing agents to form a thermoplastic foam product are each carried out as individually controlled steps thereby permitting the gel temperature to be controlled essentially independently of the throughput rate without raising the resin temperature by the work put into it. Thus, low
25 temperature continuous preparation of thermoplastic resin foam compositions at advantageous throughput rates is enhanced and assured.

30 In steps (a) through (c) of the above-mentioned method of the present invention, the temperature of the resin gel can range from about 40°C to about 150°C above the glass transition temperature (T_g) or melt temperature (T_m) of the resin, preferably from about
35 40°C to about 100°C above the T_g or T_m and more

-12-

preferably from about 50°C to about 90°C above the T_g or T_m.

5 The melting-mixing step (a) preferably includes pre-pressurizing of the resin melt to a pressure in the range from about 0.01 psig (0.07 kPag) to about 980 psig (6800 kPag), preferably from about 0.01 psig (0.07 kPag) to about 500 psig (3500 kPag), and most preferably from about 0.01 psig (0.07 kPag) to about 100 psig (700
10 kPag).

The pressure in pressurizing step (b) and the pressurizing mixing step (c) usually ranges from about 1000 psig (7000 kPag) to about 10,000 psig (70,000
15 kPag), preferably about 1000 psig (7000 kPag) to about 5000 psig (35,000 kPag), and more preferably from about 1500 psig (10,000 kPag) to about 3000 psig (21,000 kPag).

20 The conditions for cooling, depressurizing and foaming can be those commonly used in the art such as disclosed in Corbett et al., U.S. Patent No. 3,770,668 and McCurdy et al., U.S. Patent No. 2,669,751.

25 Corbett et al. discloses styrenic polymer foams and methods and apparatus for extrusion thereof. McCurdy et al. discloses an improved process for the preparation of thermoplastic foam. One feature of the improvement is a method for mixing and cooling of the
30 resin gel in a vessel downstream from an extruder.

One embodiment of an apparatus suitable for carrying out the process of the invention is shown in Fig. 1. Such apparatus can be employed for continuous
35 production of thermoplastic resin foam compositions. Included is a melting-mixing means 10 for melting at

-13-

1 last one thermoplastic resin to a liquid state and
mixing the resin to form a resin melt. It is essential
that the melting-mixing means have moving mixing
elements that are adapted by spacing between the moving
5 mixing elements and interaction thereof to accomplish
substantial mixing of the resin substantially without
sufficient shear to cause a localized temperature rise
at which substantial depredation of the resin occurs.

10 In a preferred embodiment for making resin foam
compositions the melting-mixing means 10 is adapted to
accomplish substantial mixing without sufficient shear
to cause a localized temperature rise in the temperature
15 of the resin melt to greater than about 40°C to about
150°C above the Tg or Tm of the resin, but preferably
without raising the temperature from about 40°C to about
100°C above the Tg or Tm and more preferably to no more
than about 50°C to 90°C above the Tg or Tm. The moving
20 mixing elements in melting-mixing means 10 are
preferably twin spaced apart screws each having spiral
flights thereabout.

Suitably, the mixing screws are spaced about
25 0.125 inches (in)(0.32 centimeter(cm)) to about 0.25 in
(0.65 cm) apart to avoid unwanted shear action. The
mixing screws are mounted within a chamber or vessel
having heating and cooling elements externally attached
to the chamber wall. The mixing chamber is also
30 provided with an inlet for continuous feed of
thermoplastic resin, usually in particulate or
pelletized form. The chamber at the discharge end of
the chamber is provided with an outlet 11 for discharge
of resin melt into a conduit leading to the inlet of a
35 suitable pump means 12.

-14-

The means for causing resin melt to discharge from the outlet of the melting-mixing means may be gravity flow, e.g. by vertical disposition of the mixer, or the action of the moving mixing means but preferably is a pre-pressurizing means adjacent the outlet adapted to discharge resin melt at a pressure up to about 980 psig (6800 kPag). Preferably, the pre-pressurizing means is a modified distal section of the moving mixing elements of the melting-mixing means adapted to discharge resin melt at a pressure preferably in the range of about 0.01 psig (0.07 kPag) to about 100 psig (700 kPag). The pressurized resin melt exiting the pump 12 via an outlet is led through a conduit to the inlet of pressurized mixing means 13.

A preferred melting-mixing means is a modification of a compounder or a continuous mixer as disclosed in Ahlefeld, Jr. et al., U.S. Patent No. 3,154,808.

The pump means 12 is preferably a gear pump and is used for pressurizing the resin melt to a pressure in the range of about 1000 psig (7000 kPag) to about 10,000 psig (70,000 kPag), preferably from about 1500 psig (10,000 kPag) to about 3000 psig (21,000 kPag). The pump means 12 has an outlet and means for metering resin melt through the outlet. The pump means used must be capable of handling a rather viscous resin melt and function without causing substantial temperature rise of the melt.

The pressurized mixing means 13 is used for dispersing blowing agent material into the resin melt within a pressurized zone. The pressurized mixing means may be most any mixing vessel or chamber equipped with

-15-

mixing elements and adapted to receive and mix resin melt and blowing agents under a preselected pressure in the range of about 1,000 psig (7000 kPag) to about 10,000 psig (70,000 kPag), the pressure being sufficient to maintain the blowing agents in a substantially miscible form in the melt. While the resin melt is fed continuously into the pressurized mixing means through an inlet 15 under the preselected pressure the blowing agents are continuously injected into the mixing chamber through another inlet 14. The mixing elements may for example be pins projecting in opposed directions from a cylindrical rotor and a surrounding stator, or the mixing may be accomplished with a cavity-transfer mixer with an overlapping array of cup shaped concave recesses in each of the rotor and the stator and a relatively small annular spacing. A combination of mixing means may be employed to disperse blowing agent material in the resin melt.

Preferably, the pressurized mixing means 13 of Fig. 1 is an in-line kinetic mixer, an example of which is disclosed by McCurdy et al., U.S. Patent No. 2,669,751. In another preferred embodiment the pressurized mixing means 13 comprises a cavity-transfer mixer. Cavity-transfer mixers are disclosed in Gale, U.S. Patent No. 4,419,014.

It is desirable to get substantially homogeneous dispersion of the blowing agent in the resin melt to form a resin gel while at the same time not generating excessive local heating because of mechanical work input.

It is essential to maintain a pre-selected pressure in the mixing chamber and keep the blowing

-16-

agent from forming a foam until the gel subsequently is released through a foam forming orifice.

5 The resin gel is discharged under pressure from the pressurized mixing means 13 through outlet 16 and through a conduit to the inlet of the cooling-depressurizing means 19. The cooled gel exits the cooling-pressurizing means at an outlet and enters the foam-forming die orifice means 20. After the gel leaves 10 the die orifice, the gel is formed into a foam or foamable composition. The particular shape and properties of the resin foam composition are further controlled after the gel exits the die orifice using temperature and pressure modifying means. 15

 The cooling-depressurizing means and the foam-forming die orifice means may take the form of most any of the equipment known in the art for the purpose of making foam. Entirely suitable and preferred equipment 20 is described in Corbett, U.S. Patent No. 3,770,668.

 If desired, in order to assure more uniform cell size in the foam product it may be desirable to pass the cooled resin gel, while still under pressure, 25 through a static mixer 40, or series of static mixers before releasing the pressurized gel to a reduced pressure, e.g. ambient atmospheric pressure, through a typical foam-forming die orifice. The foam forming at 30 the orifice will be directed into making foam sheets, foam boards, foam particles and other typically extruded foam compositions using the appropriate post-die forming means such as a mandrel, forming shoes, forming plates and other typical post-die orifice means as well 35

-17-

understood in the art. Foamable compositions can also be made.

In order to monitor the temperature and pressure of the resin melt and resin gel throughout the system a metering sensor means 21 connected to the output of the melting-mixing means 10 is provided; a metering sensor means 22 connected to the conduit between the pump means 12 and pressurized mixing means 13 is provided; a metering sensor means 23 connected to the conduit between the pressurized mixing means 13 and the cooling-depressurizing means 19 is provided; and a metering sensor means 24 connected to the conduit between the cooling-depressurizing means 19 and the foam-forming die orifice means 20 is provided.

Another embodiment of the apparatus production line of the invention is shown in Fig. 2, which is similar to Fig. 1 with the exception of a modification of the pressurized mixing means 13 as illustrated. A melting-mixing means 30 corresponds to the melting-mixing means 10 of Fig. 1. A pump means 32 corresponds to the pump means 12 of Fig. 1. The essential difference between the figures is that the pressurized mixing means 13 of Fig. 1 is replaced by a pressurized mixing means 33 and a second pressurized mixing means 37. Pressurized mixing means 33 comprises an in-line kinetic device such as a spline mixer and pressurized mixing means 37 comprises a cavity-transfer mixer. This arrangement of mixing devices is preferable when processing resin melts or gels at or near the T_g or T_m of the resin. In a further embodiment it may be preferable for pressurized mixing means 33 to comprise a

-18-

cavity-transfer mixer and pressurized mixing means 37 to comprise a spline mixer.

5 Example 1 - Production of High Bromine Containing
 Polystyrene Foam

Equipment

10 Fig. 1 illustrates schematically apparatus used
 in a pilot line to produce polystyrene foam compositions
 containing high levels of bromine. The melting-mixing
 means 10 is a Farrel 2CM Continuous Mixer™ brand mixer
 (Pomini Farrel Corp., Castellanza, Italy). The pump
 means 12 is a Luwa Vacorex Gear Pump™ brand gear pump
15 (Maag-Luwa Corp., Zurich, Switzerland). The pressurized
 mixing means 13 is an in-line kinetic mixing device as
 disclosed by McCurdy et al., U.S. Patent No. 2,669,751.
 The cooling-depressurizing means 19, and foam-forming
 die orifice means 20 of Fig. 1 are as disclosed in
20 Corbett et al., U.S. Patent No. 3,770,668. The optional
 static mixer mixing means 40 of Fig. 1, directly
 preceding the foam-forming die orifice is of
 conventional design and is optionally included to
 improve uniformity of foam composition.

25 The apparatus is clad substantially throughout
 by an insulating jacket and the temperature and pressure
 readings are monitored with metering and sensor means
 21, 22, 23 and 24, Fig. 1. The temperature of the
30 mixing chamber and the the mixing chamber orifice is
 controlled through the use of electric heaters and
 cooling devices and the temperatures of the remaining
 portions of the apparatus are independently controlled
35 through the use of jacket insulation standard in the
 industry.

Method

Using the equipment described above a series of polystyrene foam samples are produced containing different amounts of hexabromocyclododecane (HBCD). This fire retardant is added to the thermoplastic resin melt in proportions in the range of 1.4 weight percent to 3.3 weight percent.

Table I shows various formulations of the thermoplastic resin composition processed at a production rate of 200 lbs (90 kg) per hour. Table III shows the actual amount of fire retardant in each sample formulation.

TABLE I
Foam Composition and Feed Rate

	<u>MATERIAL</u>	<u>FEED RATE</u> <u>IN LB/HR</u>	<u>FEED RATE</u> <u>IN KG/HR</u>
20	Polystyrene (weight average MW of about 200,000)	200	91
	HBCD	Varied as indicated*	
	Magnesium Oxide	0.15	0.07
25	Talc	0.60	0.27
	Low Density Polyethylene (LDPE)	0.26	0.12
	Tetrasodiumpyrophosphate (TSPP)	0.30	0.14
	Ethyl Chloride	7.6	3.4
30	Dichlorodifluoromethane (CFC-12)	15.2	6.9
	Carbon Dioxide	2.2	1.0

*1.4 weight percent to 3.3 weight percent of the resin as represented in Table III.

-20-

Table II shows temperatures, pressures and production rates at various points in the system including the Farrel Continuous Mixer (FCM), the gear pump, and the in-line kinetic mixer (IKM).

TABLE II
PROCESS CONDITIONS

	<u>Process Temperatures deg C</u>					
	<u>Sample</u>					
	1	2	3	4	5	6
Out FCM	162.8	162.3	163.1	162.6	162.7	162.3
Out Gear Pump	164.1	163.1	164.5	163.1	164.2	163.2
Out IKM	181.8	181.5	181.8	180.9	181.6	181.1
Die	125.0	125.1	125.0	125.0	125.1	125.0
	<u>Process Pressures psig (kPag)</u>					
Out Gear Pump	2260 (15580)	2310 (15930)	2210 (15210)	2220 (15307)	2200 (15170)	2200 (15170)
Out IKM	1780 (12270)	1700 (11720)	1730 (11930)	1740 (12000)	1720 (11859)	1710 (11790)
	<u>Board Speed ft/min (m/min)</u>					
	56.4 (17.2)	57.2 (17.4)	56.5 (17.2)	57.0 (17.4)	53.2 (16.2)	55.7 (17.0)

The maximum processing resin gel temperature of any sample is under 185°C. The density of all foam product samples is approximately 2.1 lb/ft³ (33.6 kg/m³). The cell size of all foam product samples is between 0.3 and 0.4 millimeters.

Table III shows the densities and cell sizes of the samples as a measure of quality of foam product. The amount of fire retardant is varied while density and cell size remain substantially uniform and constant as demonstrated using standard ASTM testing methods.

Visual examination of various portions of the foam shows no instances of any evidence of thermal degradation of either the resin or the fire retardant.

TABLE III

5

Foam Properties as a Function of Bromine Content

	<u>Sample</u>	<u>Weight Percent HBCD in Resin</u>	<u>Weight Percent Bromine in Resin</u>	<u>Density lb/ft³ (kg/m³)</u>	<u>Cell Size (mm)</u>
10	1	1.4	.90	2.10 (33.6)	.36
	2	1.8	1.16	2.10 (33.6)	.37
	3	2.2	1.41	2.11 (33.8)	.34
15	4	2.5	1.60	2.10 (33.6)	.35
	5	2.9	1.88	2.08 (33.3)	.35
20	6	3.3	2.05	2.11 (33.8)	.35

Example 2 - Production of Rubber-Modified Polystyrene
Foam With Desirable Levels of Fire
Retardant

25

A pilot plant line corresponding to the apparatus of Example 1 is employed to produce rubber-modified polystyrene (RMPS) foam composition samples with desirably high levels of preferred fire retardant.

30

The processing is initiated with a virgin feed of polystyrene and subsequently the polymeric feed is switched to a rubber-modified polystyrene resin wherein the polystyrene is of weight average MW in the range of 200,000 +/- 1,000 and contains dispersed polymeric butadiene particles in an amount of about 8.5 weight

35

perc nt f the resin weight. The process is controlled to give a foam-forming die orifice pressure of 700 ± 100 psig (4800 ± 700 kls). The temperature in mixing chamber and at the outlet of the Farrel Continuous Mixer (FCM), the melting-mixing means 10, is maintained at about 175°C . The gear pump speed is adjusted to give output rates of about 200 lbs/hr (90 kg/hr).

The resin formulations of the seven foam samples are given in Table IV. The amount of two of the blowing agents, ethyl chloride and carbon dioxide are varied between the resin formulations as carbon dioxide is used to enhance cell nucleation. The weight percent units are based on the weight of RMPS.

TABLE IV
FORMULATION DATA

			<u>Samples</u>						
	<u>Resin</u> <u>Composition</u>	<u>Units</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>
5	RMPS	lb/hr	200	200	200	200	200	200	200
		kg/hr	90	90	90	90	90	90	90
	HBCD	weight percent	1.6	1.6	1.6	1.6	1.6	1.6	1.6
10	Talc - 15% Conc. in polystyrene	weight percent	0.4	0.4	0.4	0.4	0.4	0.4	0.4
	Magnesium Oxide	weight percent	0.1	0.1	0.1	0.1	0.1	0.1	0.1
15	Difluorodi- chloromethane	weight percent	6.1	6.1	6.1	6.1	6.1	6.1	6.1
	Ethyl Chloride	weight percent	4.0	2.6	2.6	2.6	2.6	2.6	2.6
	Carbon Dioxide	weight percent	1.1	2.0	2.9	2.4	2.9	2.4	2.9

20

The process variables used to produce the seven foam samples are listed in Table V.

25

30

35

TABLE V
PROCESS VARIABLES

		<u>Samples</u>						
	<u>Units.</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>
Feed Rate of	lb/hr	200	200	200	200	200	200	200
RMPS	kg/hr	90	90	90	90	90	90	90
Sample Width	inch	5.8	4.6	4.3	4.6	4.6	3.7	4.1
	mm	147	117	109	117	117	94	104
Sample Thickness°	inch	1.0	0.9	0.9	0.9	0.8	0.8	0.9
	mm	25	23	23	23	20	20	23
Board Speed	ft/min	--	--	79	67	75	95	--
	m/min	--	--	24	20	23	29	--
<u>System Temperatures</u>								
Out FCM	°C	169	170	171	170	170	170	170
Out Gear Pump	°C	169	169	171	171	170	171	170
Out IKM	°C	191	190	190	191	189	190	189
<u>System Pressures</u>								
FCM Outlet	psig	<10	<10	<10	<10	<10	<10	<10
	kPag	<69	<69	<69	<69	<69	<69	<69
Gear Pump Outlet	psig	2720	2510	2530	2750	2680	2550	----
	kPag	18,750	17,310	17,440	18,960	18,480	17,580	----

30 The density and cell size for the resultant foam samples are shown in Table VI. The density ranges from about 1.4 lb/ft³ (22.4 kg/m³) to about 2.3 lb/ft³ (36.8 kg/m³) and the cell size ranges from about 0.5 mm to about 1.7 mm in diameter. These results indicate that blowing agent efficiency is maintained. No evidence of thermal degradation of resin or fire retardant is found in any of the samples upon visual examination.

TABLE VIFOAM PROPERTY DATA

	<u>Sample</u>	<u>Units</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>
5	Density								
	ASTM Test	lb/ft ³	2.30	1.74	1.63	1.80	1.81	1.66	1.38
	D-1622	kg/m ³	36.8	27.9	26.1	28.8	29.0	26.6	22.1
	Cell Size								
	ASTM Test								
	D-3176	mm	1.74	0.79	0.57	0.59	0.58	0.63	0.50

10

Example 3 - Apparatus for Production of Polystyrene Foam
Under Low Temperature Conditions

Utilizing the apparatus of Fig. 2, a thermoplastic
 15 polystyrene resin foam composition is produced utilizing
 as the melting-mixing means 30 a Farrel FCM Continuous
 Mixer™ brand mixer, model 6UM (Farrel Company, Ansonia,
 CT); as the pump means 31, a Luwa Vacorex Gear Pump™
 brand gear pump (Maag-Luwa Corp., Zurich, Switzerland);
 20 as the pressurized mixers 33 and 37 in tandem, an in-
 line kinetic mixer as disclosed in McCurdy et al., U.S.
 Patent No. 2,669,751 and a cavity-transfer mixer; a
 conventional cooling-depressurizing means 39 such as
 that disclosed in Corbett et al., and a conventional
 25 foam-forming die orifice means 41.

Resin and additives listed in Table IX are fed
 into the mixing chamber of the melting-mixing means 30.
 The blowing agents, introduced into the first
 30 pressurized mixing means 33 at point 36 are about
 7 percent by weight of difluorodichloromethane, about
 1.5 percent by weight CO₂ and about 3 percent by weight
 ethyl chloride, based on the total resin gel
 35 composition.

The preferred operating temperature range is about 140°C to about 195°C. The resin melt temperature is about 140°C to about 185°C. The resin gel temperature is about 150°C to about 190°C. The gear pump input pressure is about 0.01 psig (0.07 kPag) to about 50 psig (350 kPag). The gear pump output pressure is about 1500 psig (10,300 kPag) to about 2500 psig (17,200 kPag).

No evidence of thermal degradation is found in the product.

TABLE IX
RESIN FORMULATION

	<u>Ingredient</u>	<u>Weight %</u>
15	Polystyrene (about 200,000 MW)	about 84.045% by weight
	HBCD	3.0%
	Magnesium Oxide	0.015%
	TSPP	0.15%
20	LDPE	0.1%
	Barium or Calcium Stearate	0.15%
	Talc	1.0%

25

30

35

CLAIMS

1. A continuous method of preparation of a thermoplastic resin foam or foamable composition comprising sequentially the steps of:

5 (a) melting and mixing at least one thermoplastic resin to form a resin melt, the mixing process being carried out without applying shear forces of sufficient thermal energy to cause a localized rise in temperature of the resin melt to a temperature at which substantial degradation of the resin occurs;

10 (b) pressurizing to and maintaining the resin melt at a pressure sufficient to permit introduction of one or more blowing agents into the resin melt at a temperature below the temperature at which substantial degradation of the resin melt occurs;

15 (c) introducing and dispersing the one or more blowing agents substantially throughout the resin melt to form a resin gel at a temperature above the glass transition temperature or the melt temperature of the thermoplastic resin and below a temperature at which
20 substantial degradation of the resin gel occurs; and

25 (d) cooling and depressurizing the resin gel, the depressurizing being carried out at a sufficiently cool temperature for formation of a foam or foamable

composition with structural integrity, and the cooling and depressurizing being carried out substantially at the same time;

- (e) either foaming and forming the resin gel
5 to form a solid foam composition or foaming the resin gel to form a solid foamable composition;

the recited steps being carried out continuously in a series of stages with the temperature
10 of the resin melt and gel being maintained substantially independently of the flow rate of the resin melt and gel advancing through and between the stages.

2. A method as claimed in Claim 1, wherein
15 the resin is selected from polystyrene, rubber-modified polystyrene, and rubber-modified polyethylene.

3. A method as claimed in Claim 2, wherein the resin is selected from rubber modified polystyrene
20 or polyethylene containing 3 to 30 weight percent (based on total resin weight) dispersed polymeric butadiene particles.

4. A method as claimed in any one of the
25 preceding claims, wherein the resin contains 0.01 to 5 weight percent (based on total resin weight) of a fire-retardant.

5. A method as claimed in Claim 4 wherein the
30 fire retardant is selected from hexabromocyclododecane, pentabromomonochlorocyclohexane and tetrabromobisphenol A.

6. A method as claimed in any one of the preceding claims, wherein the resin melt is pr -

pressurized prior to step (b) to a pressure range from 0.07 kPag (0.01 psig) to 7,000 kPag (980 psig).

7. A method as claimed in any one of the preceding claims, wherein the pressure of step (b) is
5 from 7,000 kPa (1000 psig) to 70,000 kPa (10,000 psig).

8. An apparatus for continuous production of thermoplastic resin foam or foamable compositions by a method as claimed in Claim 1, said apparatus comprising:

10 (a) melting-mixing means for melting and mixing a resin to form a resin melt, the melting-mixing means having moving mixing elements and being adapted by the spacing between the moving mixing elements and
15 interaction thereof to accomplish substantial mixing of the resin melt essentially without shear forces of sufficient thermal energy to cause a localized temperature rise in the temperature of the resin melt to greater than 150°C above the glass transition
20 temperature or the melt temperature of the resin, the melting-mixing means having an inlet for the resin and an outlet for the resin melt, and means for causing the resin melt to discharge from the outlet;

25 (b) pump means for pressurizing the resin melt to a pressure in the range of 7,000 kPa (1000 psig) to 70,000 kPa (10,000 psig), the pump means having an inlet and an outlet and means for metering the resin melt
30 through the outlet;

(c) pressurized mixing means for dispersing blowing agents in the resin melt within a pressurized zone to form a resin gel, the pressurized mixing means being provided with an inlet for introducing the blowing

agents, an inlet for the resin melt, and an outlet for discharging the resin gel under pressure;

(d) cooling-depressurizing means for concurrently cooling and depressurizing the resin gel to a temperature and pressure sufficient for discharging the resin gel through a foam-forming die orifice means; the cooling-depressurizing means having an inlet for receiving the resin gel under pressure and an outlet for the cooled gel; and

(e) conduit means providing fluid communication respectively and sequentially between the outlet of the melting-mixing means and the inlet of the pump means, between the outlet of the pump means and the inlet of the pressurized mixing means, between the outlet of the pressurized mixing means and the inlet of the cooling-depressurizing means and between the outlet of the cooling-depressurizing means and the foam-forming die orifice means.

9. An apparatus as claimed in Claim 8, wherein the moving mixing elements of the melting-mixing means are twin spaced-apart screws having spiral flights thereabout.

10. An apparatus as claimed in Claim 8 or Claim 9, wherein the pre-pressurizing means comprises a modified distal section of the moving mixing elements of the melting-mixing means.

11. An apparatus as claimed in any one of Claims 8 to 10, wherein the pump means comprises a gear pump.

12. A thermoplastic foam composition comprising a resin selected from the group consisting of: rubber-modified polystyrene resin and rubber-modified polyethylene resin; and 0.01 weight percent to 5 weight percent by resin weight of a fire retardant wherein the resin has 3 weight percent to 30 weight percent rubber based on total resin weight.

10

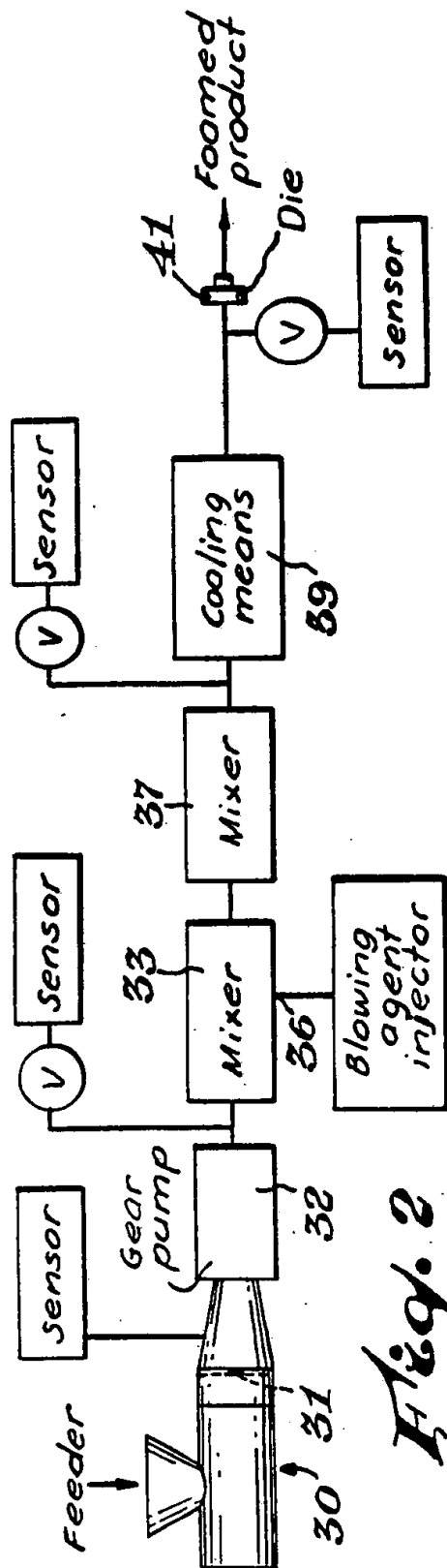
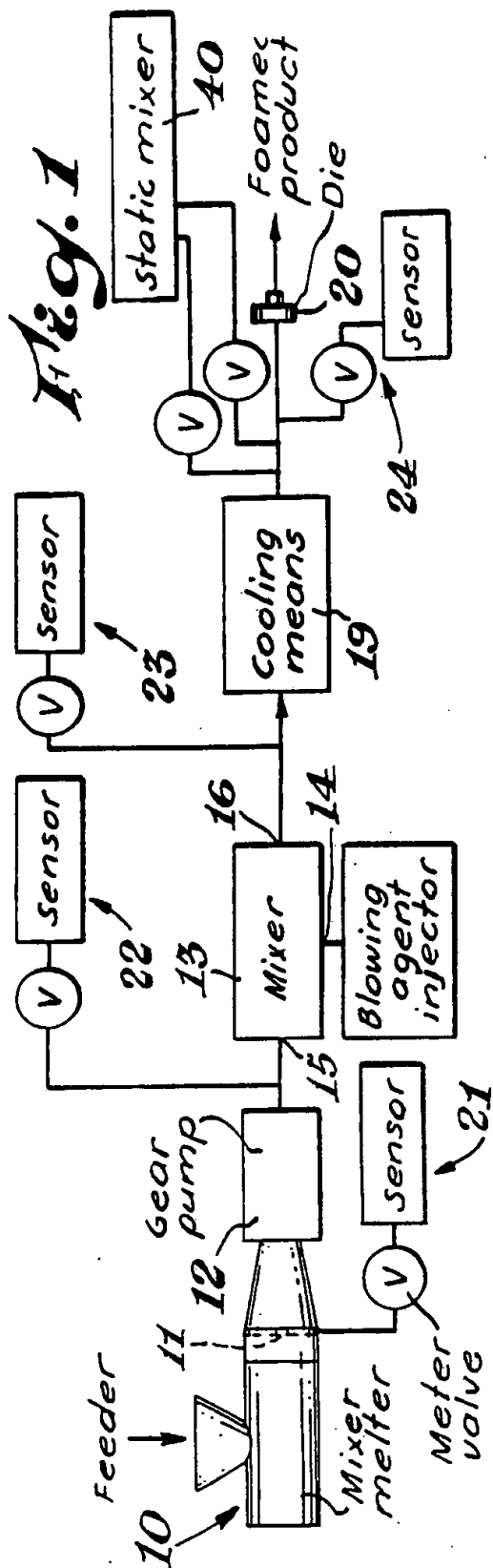
15

20

25

30

1/1



INTERNATIONAL SEARCH REPORT

International Application No. PCT/US89/05865

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC(5) B29B 7/30, 7/32, 7/46; C08J 9/12, 9/14, 9/30 US CL 264/53; 425/4C, 366, 378.1, 817C; 521/79, 81, 139, 140																													
II. FIELDS SEARCHED <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black; margin: 5px 0;">Minimum Documentation Searched ⁷</div> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 25%; border: 1px solid black; text-align: left;">Classification System</th> <th style="border: 1px solid black; text-align: left;">Classification Symbols</th> </tr> <tr> <td style="border: 1px solid black; text-align: center; vertical-align: top;">U.S.</td> <td style="border: 1px solid black; vertical-align: top;">264/53; 425/4C, 366, 378.1, 817C; 521/79, 81, 139, 140</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black; margin: 5px 0;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸</div>			Classification System	Classification Symbols	U.S.	264/53; 425/4C, 366, 378.1, 817C; 521/79, 81, 139, 140																							
Classification System	Classification Symbols																												
U.S.	264/53; 425/4C, 366, 378.1, 817C; 521/79, 81, 139, 140																												
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹ <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 10%; border: 1px solid black; text-align: left;">Category [*]</th> <th style="border: 1px solid black; text-align: left;">Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²</th> <th style="border: 1px solid black; text-align: left;">Relevant to Claim No. ¹³</th> </tr> <tr> <td style="border: 1px solid black; text-align: center; vertical-align: top;">X</td> <td style="border: 1px solid black; vertical-align: top;">US, A, 4,436,679 (WINSTEAD) 13 March 1984 See entire document</td> <td style="border: 1px solid black; vertical-align: top;">1-11</td> </tr> <tr> <td style="border: 1px solid black; text-align: center; vertical-align: top;">X</td> <td style="border: 1px solid black; vertical-align: top;">US, A, 3,830,901 (WINSTEAD) 20 August 1974 See entire document</td> <td style="border: 1px solid black; vertical-align: top;">1-11</td> </tr> <tr> <td style="border: 1px solid black; text-align: center; vertical-align: top;">Y</td> <td style="border: 1px solid black; vertical-align: top;">US, A, 4,615,664 (KOLOSSOW) 07 October 1986 See entire document</td> <td style="border: 1px solid black; vertical-align: top;">1-11</td> </tr> <tr> <td style="border: 1px solid black; text-align: center; vertical-align: top;">Y</td> <td style="border: 1px solid black; vertical-align: top;">US, A, 4,469,651 (HAHN ET AL.) 04 September 1984 See entire document</td> <td style="border: 1px solid black; vertical-align: top;">1-11</td> </tr> <tr> <td style="border: 1px solid black; text-align: center; vertical-align: top;">Y</td> <td style="border: 1px solid black; vertical-align: top;">US, A, 4,454,087 (HAYASHI ET AL.) 12 June 1984 See entire document</td> <td style="border: 1px solid black; vertical-align: top;">1-11</td> </tr> <tr> <td style="border: 1px solid black; text-align: center; vertical-align: top;">Y</td> <td style="border: 1px solid black; vertical-align: top;">US, A, 4,560,334 (RUTLEDGE) 24 December 1985 See entire document</td> <td style="border: 1px solid black; vertical-align: top;">1-11</td> </tr> <tr> <td style="border: 1px solid black; text-align: center; vertical-align: top;">Y</td> <td style="border: 1px solid black; vertical-align: top;">US, A, 4,299,792 (NUNN) 10 November 1981 See entire document</td> <td style="border: 1px solid black; vertical-align: top;">1-11</td> </tr> <tr> <td style="border: 1px solid black; text-align: center; vertical-align: top;">A</td> <td style="border: 1px solid black; vertical-align: top;">US, A, 2,515,250 (McINTIRE) 18 July 1950</td> <td style="border: 1px solid black; vertical-align: top;">1-11</td> </tr> </table> <div style="margin-top: 10px;"> <div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>[*] Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p> </div> </div> </div>			Category [*]	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	X	US, A, 4,436,679 (WINSTEAD) 13 March 1984 See entire document	1-11	X	US, A, 3,830,901 (WINSTEAD) 20 August 1974 See entire document	1-11	Y	US, A, 4,615,664 (KOLOSSOW) 07 October 1986 See entire document	1-11	Y	US, A, 4,469,651 (HAHN ET AL.) 04 September 1984 See entire document	1-11	Y	US, A, 4,454,087 (HAYASHI ET AL.) 12 June 1984 See entire document	1-11	Y	US, A, 4,560,334 (RUTLEDGE) 24 December 1985 See entire document	1-11	Y	US, A, 4,299,792 (NUNN) 10 November 1981 See entire document	1-11	A	US, A, 2,515,250 (McINTIRE) 18 July 1950	1-11
Category [*]	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³																											
X	US, A, 4,436,679 (WINSTEAD) 13 March 1984 See entire document	1-11																											
X	US, A, 3,830,901 (WINSTEAD) 20 August 1974 See entire document	1-11																											
Y	US, A, 4,615,664 (KOLOSSOW) 07 October 1986 See entire document	1-11																											
Y	US, A, 4,469,651 (HAHN ET AL.) 04 September 1984 See entire document	1-11																											
Y	US, A, 4,454,087 (HAYASHI ET AL.) 12 June 1984 See entire document	1-11																											
Y	US, A, 4,560,334 (RUTLEDGE) 24 December 1985 See entire document	1-11																											
Y	US, A, 4,299,792 (NUNN) 10 November 1981 See entire document	1-11																											
A	US, A, 2,515,250 (McINTIRE) 18 July 1950	1-11																											
IV. CERTIFICATION <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; border: 1px solid black; vertical-align: top;"> Date of the Actual Completion of the International Search <div style="text-align: center; font-weight: bold;">14 MARCH 1990</div> </td> <td style="width: 50%; border: 1px solid black; vertical-align: top;"> Date of Mailing of this International Search Report <div style="text-align: center; font-weight: bold; font-size: 1.2em;">02 APR 1990</div> </td> </tr> <tr> <td style="border: 1px solid black; vertical-align: top;"> International Searching Authority <div style="text-align: center;">ISA/US</div> </td> <td style="border: 1px solid black; vertical-align: top;"> Signature of Authorized Officer <div style="text-align: center;"> MORTON FOELAK </div> <div style="text-align: right; margin-top: 10px;"> HO NGUYEN </div> </td> </tr> </table>			Date of the Actual Completion of the International Search <div style="text-align: center; font-weight: bold;">14 MARCH 1990</div>	Date of Mailing of this International Search Report <div style="text-align: center; font-weight: bold; font-size: 1.2em;">02 APR 1990</div>	International Searching Authority <div style="text-align: center;">ISA/US</div>	Signature of Authorized Officer <div style="text-align: center;"> MORTON FOELAK </div> <div style="text-align: right; margin-top: 10px;"> HO NGUYEN </div>																							
Date of the Actual Completion of the International Search <div style="text-align: center; font-weight: bold;">14 MARCH 1990</div>	Date of Mailing of this International Search Report <div style="text-align: center; font-weight: bold; font-size: 1.2em;">02 APR 1990</div>																												
International Searching Authority <div style="text-align: center;">ISA/US</div>	Signature of Authorized Officer <div style="text-align: center;"> MORTON FOELAK </div> <div style="text-align: right; margin-top: 10px;"> HO NGUYEN </div>																												

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

A	US, A, 2,023,204 (MUNTERS ET AL.) 03 December 1935 See entire document	1-11
X	US, A, 4,370,378 (ZABROCKI ET AL.) 25 January 1983 See entire document	12
A	US, A, 3,959,197 (SALYER ET AL.) 25 May 1976 See entire document	1-11
X	US, A, 4,198,486 (MYLICH ET AL.) 15 April 1980 See entire document	12
Y	US, A, 4,207,402 (SPEENKLE, JR.) 10 June 1980 See entire document	12

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE¹

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers _____, because they relate to subject matter ^{1,2} not required to be searched by this Authority, namely:

2. ☐ Claim numbers _____, because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out ^{1,2}, specifically:

3. ☐ Claim numbers _____, because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. ☒ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING²

This International Searching Authority found multiple inventions in this international application as follows:

(Telephone practice, see attachment)

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

- ☐ The additional search fees were accompanied by applicant's protest.
☐ No protest accompanied the payment of additional search fees.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
X	US, A, 4,323,655 (DIGIULIO ET AL.) 06 April 1982 See entire document	12
X	US, A, 4,439,547 (DIGIULIO ET AL.) 27 March 1984 See entire document	12
P,X	US, A, 4,851,453 (WHITE ET AL.) 25 July 1989 See entire document	12
X	US, A, 4,762,861 (BOHEN ET AL.) 09 August 1988 See entire document	12
P,X	US, A, 4,812,484 (ENDO ET AL.) 14 March 1989 See entire document	12
P,X	US, A, 4,849,473 (CIGNA ET AL.) 18 July 1989 See entire document	12
X	US, A, 3,669,923 (HINTZ) 13 June 1972 See entire document	12
X	US, A, 4,246,211 (KUHNEL) 20 January 1981 See entire document	12

OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING

- I. Claims 1-11 are drawn to a continuous method of making a resin foam by extrusion and an apparatus for carrying out said process and would be classified in class 264 subclass 53 and class 423 subclass 4C.
- II. Claim 12 is drawn to a rubber modified resin foam containing a flame retardant and is classified in class 521 subclass 139.

These distinct and independant inventions lack unity of invention and fail to comply with the combinations permitted by PCT Rule 13.2 (i) - (iii).

The process and apparatus claims are not limited to "an" independent claim "specifically adopted for the manufacture of the product".

The product could be produced by a materially different process and apparatus such as by an injection molding process and apparatus.